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A Feasibility Study of Ion Implantation Techniques for Mass Spectrometer Calibration

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A Feasibility Study of Ion Implantation Techniques for Mass Spectrometer Calibration

M. E. Koslin, G. A. Krycuk,
J. G. Schatz, Jr., and F. A. White
Rensselaer Polytechnic Institute
Troy, New York

G. M. Wood
Langley Research Center
Hampton, Virginia

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and Space Administration

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SUMMARY

An experimental study was undertaken to examine the feasibility of using ion implanted filaments doped with either an alkali metal or noble gas for *in situ* recalibration of onboard mass spectrometers during extended space missions. Implants of rubidium and krypton in rhenium ribbon filaments prepared at the NASA Langley Research Center were subsequently tested at Rensselaer Polytechnic Institute (RPI) in a bakeable 60° sector mass spectrometer operating in the static mode. Surface ionization and electron impact ion sources were both used, each yielding satisfactory results. The metallic implant with subsequent surface ionization provided a means of mass scale calibration and determination of system operating parameters, whereas the noble gas thermally desorbed into the system was more suited for partial pressure and sensitivity determinations.

INTRODUCTION

It is generally recognized that mass spectrometry is one of the most productive and sensitive analytical tools for determining the composition of the terrestrial atmosphere, planetary atmospheres, and the chemical composition of planetary surfaces. Variations of both chemical and isotopic composition provide an invaluable insight into geochronology and a broad spectrum of space-related studies. A wide variety of mass spectrometers suitable for use in space vehicles have been engineered and the problems of telemetering the acquired data have been generally solved.

A long-standing difficulty with instruments while positioned in space has been the lack of a satisfactory method for recalibration. Such a method is very desirable inasmuch as long periods of time may intervene between final testing and application. The use of containers of reference gases is limited because of weight considerations and by the necessity of depending on the operation of electromechanical valves, which are subject to leakage and failure in the outer space environment.

For mass spectrometers using an electron bombardment ion source, normalization of the sensitivities of various species to that of a reference specie, for example, normal butane, is an established procedure to correct for instrumental drift. One can, therefore, correct for these changes by measurement of a single specie if the calibration coefficients for the gases of interest have previously been determined and normalized to the calibration coefficient of the reference gas.

This study was undertaken to evaluate ion implantation technology with respect to its relevance and reliability for mass spectrometric calibration. It was conceived that relative calibration of the mass spectrometer could be obtained by utilizing thin rhenium ribbons which had been doped to known concentrations of a selected species by ion implantation. The ribbon would func-

tion as a thermal ion source if a metallic dopant was used or as a gas reservoir for an electron impact ion source, whereby a quantitative number of atoms could be stored and subsequently released in the gaseous phase by simply heating the ribbon to some preselected temperature. These small doped ribbons integrated into the mass spectrometer ion source could therefore be heated on command to provide real time correction of data.

Metallic species are, in general, not depleted by a single heating of the host (ref. 1), so that a single ribbon may be used a number of times. Noble gases will, on the other hand, be completely desorbed; thus, a number of ribbons equal to the number of calibrations to be performed is necessary. Repeatability in number density of the desorbed noble gas atoms from successively heated filaments is obtained by simultaneously implanting a number of filaments with the gaseous specie.

DESCRIPTION OF APPARATUS

An all-metal mass spectrometer (ref. 2), bakeable to 400° C, was used for the experiments. (See fig. 1.) Figure 2 is a schematic diagram of the mass spectrometer and the pumping system used to establish the ultimate base pressure prior to placing the system in the static operational mode. Base pressures obtained were of the order of 10^{-8} torr (1 torr = 133.3 Pa). Cleanliness of the system was maintained through the use of sorption pumps, ion pumps, and liquid nitrogen trapping as shown in the schematic. The static mode of operation enables virtually all the sample gas to be retained within the mass spectrometer tube for analysis by completely sealing off the analyzer section from dynamic pumping while data are being obtained. Also, the known quantity of implanted gas can be considered to be an "isotopic spike" and quantitative determinations of the gaseous composition can be made by utilizing the isotopic dilution method for determining trace concentrations.

The mass spectrometer is a 60° magnetic sector type with a nominal 15.24-cm (6-in.) radius of curvature. The source and detector housings of the mass spectrometer as well as the analyzer section were fabricated from type 304 nonmagnetic stainless steel. Commercially available stainless steel crosses with 6.99-cm (2.75-in.) O.D. flanges form a gas handling system. All the flanges in the spectrometer are metal seal types using oxygen-free high-conductivity copper gaskets. Metal seal valves were used for isolation of the spectrometer and also between the various segments of the system. These valves were bakeable to 450° C when open and to 250° C when closed.

Electrical feedthroughs for the ion source were bonded ceramic-to-metal pins brazed on two 6.99-cm (2.75-in.) flanges. To allow for installation of external resistors for the electron multiplier, a special 16-pin feedthrough on a 10.16-cm (4-in.) O.D. flange was fabricated. Both source and multiplier feedthroughs were designed for use under extended bakeouts.

An 80-liter-per-second sputter ion pump was used to obtain the system ultimate pressure. To suppress gas backstreaming, a liquid nitrogen trap was added above the pump. This trap also provided additional pumping speed for condensa-

ble gases and served to reduce fringing field effects from the ion pump magnet by locating the pump further from the ion beam region.

For roughing the system, a rotary oil-sealed mechanical pump was employed until the onset of molecular flow. Then a zeolight-filled sorption pump cooled with liquid nitrogen (LN_2) pumped the system to below 10^{-4} torr where the ion pump was started. This sorption pump was also employed during bakeout to remove the evolved gas. To protect against rough pump oil backstreaming, a molecular sieve was included between the rough and sorption pumps. The gas handling system had its own sorption-pump—rough-pump combination so that samples could be changed without bringing the entire system up to high pressure.

Prior to assembly, all parts were scrubbed with benzene and/or detergent to remove gross surface contamination and were cleaned in sequential ultrasonic baths with high purity benzene, ethyl alcohol, and deionized water. A final thorough rinsing in pure deionized water was followed by drying under an infrared lamp in a laminar flow hood to prevent dust from collecting on the cleaned surfaces. The solvents were utilized in the stated order because each dissolves in the subsequent solvent. Alcohol was selected over acetone, although less volatile, because it was known to leave less residue on the surfaces.

Two separate ion sources were designed and fabricated for the system. The first is a thermal ionization source with collimators and an ion accelerating plate, but without subsequent focusing electrodes. (See fig. 3.) Atoms diffusing to the surface of the heated ribbon filament are emitted as ions if the atomic ionization potential is less than the work function of the filament. The ion yield is temperature dependent and is given by the Saha-Langmuir equation

$$\frac{n^+}{n^o} = C \exp e \frac{(\phi - I)}{kT}$$

where n^+ and n^o are the ionic and neutral flux densities from the surface; ϕ is the surface work function; I, the ionization potential; k, the Boltzmann constant; e, the electronic charge; T, the absolute temperature of the surface; and C, a constant.

The second, a Nier-type electron impact source (fig. 4) in which ions are created through interaction of the atoms with a collimated beam of electrons, was used to ionize the gaseous species. This type of source includes several focusing electrodes to compensate for magnetic field effects, and collimation slits for beam shaping and positioning.

Ribbon filaments implanted with krypton were spotwelded to a high vacuum electrical feedthrough as shown in figure 5. This arrangement provided a means by which each of the filaments could be resistively heated in succession to release the implanted krypton into the mass spectrometer.

The detection system consisted of a 14-stage electron multiplier having a gain of approximately 10^6 at 3000 volts. The analog current was measured at the collector by a picoammeter. An alternative mode of ion detection was to count individual ions in a pulse counting mode with appropriate circuitry (ref. 3), but for most of the measurements the use of the counting system was

not required because of the magnitude of the ion currents obtainable from the implanted filaments.

EXPERIMENTS AND RESULTS

Mass Spectrometer Calibration

The thermal ionization source (fig. 3) was first utilized to establish an accurate mass scale, and subsequently to provide an overall determination of the system operating parameters. A rhenium filament was implanted with rubidium which has two naturally occurring isotopes, ^{85}Rb and ^{87}Rb with relative abundances of 72.15 percent and 27.85 percent, respectively. This element has a low first ionization potential (4.18 eV). Its mass number is intermediate between the light gases and the heavy metals.

The efficiency of rhenium for use in surface ionization sources has been discussed in the literature by McHugh (ref. 4) and others. For polycrystalline surfaces, the average value of the work function for surface ionization is weighted toward the number of high work function single crystal patches occurring on the polycrystalline surface. In the case of rhenium, the maximum work function occurs for the (0001) plane, and falls between 5.6 and 5.8 eV, depending upon the method used for measurement. Since a large number of the basal (0001) planes are exposed on the surface of the annealed material, the average work function for rhenium is approximately 5.1 to 5.3 eV, which is sufficiently higher than the ionization potential of rubidium at 4.18 eV to produce easily measurable ion currents.

The rubidium doping of the rhenium ribbon filaments used in the experiment was accomplished by two techniques. First, rhenium filaments were ion implanted at the NASA Langley Research Center in the ion implantation facility (ref. 1, pp. 139-140) at 40 keV to an area concentration of 2×10^{16} Rb^+/cm^2. Secondly, ribbon filaments were doped by standard chemical procedures (ref. 5, p. 66), whereby a solution of rubidium chloride was micropippetted onto the filament surface and evaporated to dryness. A spectrum of rubidium obtained in the static mass spectrometer is shown in figure 6, corresponding to the natural isotopic abundance (ref. 5, p. 340) of this element. Ion current levels at the detector were of the order of 10^{-12} amperes for this data demonstrating that readily measurable ion currents can be obtained from the ion-implanted filaments. For smaller quantities of material, comparable spectra are obtainable at current levels of the order of 10^{-16} amperes, corresponding to approximately 10^{-17} grams of mass resolved ions at the detector.

The chemically doped filaments were examined to determine whether preparation of the filaments in this manner would be applicable to this use since no special equipment is required. For calibration purposes, however, the ion-implanted filaments were substantially superior to the chemically doped samples. First, a relatively constant beam of ions was obtained over a period of days. Secondly, the ion-implantation technique precluded any loss of the sample from the surface by vibration, abrasion, or oxidation, etc. Further, it has been shown that a diffusion-surface ionization source (ref. 6), which is best exem-

plified by ion implantation, serves to conserve the sample and yield a pure atomic beam rather than a molecular beam.

As stated above, despite the relatively small amount of sample in the ion-implanted filaments, readily measurable ion current levels were obtained over a wide range of temperatures over extended periods of time. One such sample was run intermittently for a period of 2 weeks and demonstrated that at least for low ionization potential metals, ion-implantation technology provides a stable and sensitive method for providing the relative calibration capability desired. Order of magnitude ion-emission rates typical of those obtained from the ion-implanted samples are shown in figure 7. Similar data obtained from cesium ion (Cs 133) implanted in tungsten also showed prolific ion beams that at low current levels lasted as long as a week in continuous emission. This result confirmed the fact that recovery of ion-implanted metallic species appeared to be better suited for this purpose than the recovery and analysis of samples by other methods.

It should be explicitly stated that although the emission of alkali metal ions from the rhenium filament may be used for sensitivity determinations if certain conditions are met, it is suggested that it is better suited for instrument tuning and mass scale determinations because of the dependence of the ion-emission rate on the temperature and the work function of the emitting surface. Although the temperature dependence of the average work function itself is slight, an increase due to the formation of oxides on the filament surface is, in general, not insignificant (ref. 7) and is temperature dependent. Chemical reactions of the adsorbed oxygen and the ionizing species may also occur; as a result, a fraction of the atoms are emitted as oxides. Therefore, unless extremely pure surface conditions are maintained as was done in the experiment described here, deviations in ion beam intensity will occur that cannot readily be differentiated from changes in sensitivity of the mass spectrometer. In the absence of halogens, the use of ion-implanted cesium in platinum or 0.92Pt-0.08W alloy ribbon should minimize the problem of sensitivity determinations since the work function remains stable in the presence of nitrogen or oxygen (ref. 8), and the ionization efficiency approaches unity over a wide temperature range.

Partial Pressure Analysis

The electron impact source was used to obtain a residual gas analysis and to determine the feasibility of using argon and krypton for both calibration and partial pressure measurements. Clearly, noble gases must be used for this purpose rather than others which would tend to adsorb on surfaces of the analyzer. The spectrum displayed in figure 8 showed that the region around krypton was relatively background free. Although argon might not be precluded for use in outer space experiments, in general, the argon region always shows a substantial background around ^{40}Ar. The naturally occurring abundance of argon (0.93%) is so large (table I) that predictably the ion-implanted argon filaments failed to yield useful spectra for the singly charged species. The large mass peak at mass 28 (CO) appeared in all spectra and this peak could ostensibly be used as a mass marker, but the peak amplitude is highly variable.

Hence, krypton was selected as the test specie for partial pressure calibration. It is a noble gas which does not adsorb on or react with stainless steel; further, its naturally occurring terrestrial abundance is only 1×10^{-4} percent, that is, 1 ppm. The ionization potential of 13.99 eV is close to that of other gases and the position in the mass spectrum in general does not conflict with other gases of interest.

A number of rhenium filaments mounted in a target holder for simultaneous implanting of krypton in the NASA Langley facility are shown in figure 9. Prior to mounting, the filaments were flashed to high temperatures to desorb gases both from the surface and the bulk. A thin layer of gold was then deposited on the surface by radio frequency (rf) sputtering, so that the krypton ions were subsequently implanted within the gold layer. Since gold is chemically inert, adsorption of contaminants is minimal; thereby the background from the heated filament is minimized.

In preparation for analysis, all pumps were valved off so that the system would be in a static mode, and a background mass spectra was obtained. (See fig. 10(a).) The filament was then resistively heated to greater than 1500° C to ablate the gold and release the krypton. After allowing 5 minutes for pressure stabilization, a scan of the mass spectra was taken over the krypton region and appears in figure 10(b), on a scale 20 times greater than that of figure 10(a). The peak in figure 10(b) is a superposition of the isotopes of krypton appearing at mass to charge ratio (m/e) of 78, 80, 82, 83, 84, and 86. Figure 10 illustrates that krypton is a suitable candidate for partial pressure measurements and calibration because the amount of krypton emitted and detected from a single filament was at least 20 times greater than that of the background.

Since the filaments had been simultaneously implanted, the number densities of released atoms from successive tests were equivalent within the accuracy of the measurement system. Therefore, measurement of the peak height or, more accurately, the area under the curve provides a means of determining the sensitivity for the test species at some later time with respect to the sensitivity determined during final testing of the instrument.

CONCLUDING REMARKS

From the results of this feasibility study, it is evident that an ion-implanted specie can serve as a viable option for both operational testing and for the quantitative measurement of the partial pressure of gases in space-related applications. It would also appear that partial pressures as low as 10^{-10} torr can be measured inasmuch as there is no great difference in the ionization potential of krypton from that of other gases and these differences are amenable to normalization. Ion-implanted filaments can be prepared that have useful lives of years inasmuch as there is little loss of even shallow implanted species at normal temperatures.

The metallic species implants have been shown to yield prolific beams when thermally ionized for use in determining mass scale and other system operating parameters. The gaseous species implant can provide a direct means of deter-

mining shifts in instrument sensitivity and partial pressures of constituent gases when appropriate statistics are applied.

Langley Research Center
National Aeronautics and Space Administration
Hampton, VA 23665
April 5, 1978

REFERENCES

1. Wood, George Marshall, Jr.: A Mass Spectrometric System for Analyzing Thermal Desorption Spectra of Ion-Implanted Argon and Cesium in Tungsten. Ph. D. Thesis, Rensselaer Polytech. Inst., 1974.

2. Merrill, Guy L., Jr.: A Static Mode Mass Spectrometer for the Measurement of Noble Gases. Int. J. Mass Spectrom. & Ion Phys., vol. 13, no. 3, Mar. 1974, pp. 281-290.

3. Krycuk, G.; and Walling, J. D.: Miniature Charge Sensitive Preamp-Amplifier for Use With Silicon Surface Barrier Detectors. IEEE Trans. Nucl. Sci., vol. NS-20, no. 1, Feb. 1973, pp. 228-229.

4. McHugh, James A.: Surface Ionization - The Rhenium V-Type Single Filament. Int. J. Mass Spectrom. & Ion Phys., vol. 3, no. 3/4, Oct. 1969, pp. 267-276.

5. White, F. A.: Mass Spectrometry in Science and Technology. John Wiley & Sons, Inc., c.1968.

6. Rec, John R.; Myers, Willard G.; and White, Frederick A.: Diffusion Controlled, Thermal Ionization Source for Mass Spectrometric Analysis of Trace Metals. Anal. Chem., vol. 46, no. 9, Aug. 1974, pp. 1243-1247.

7. Weiershausen, W.: The Influence of Oxygen on the Surface Ionization of Some Rare Earth Metals on Tungsten and Rhenium. Advances in Mass Spectrometry, Volume 3, W. L. Mead, ed., Elsevier Publ. Co. (Amsterdam), 1966, pp. 755-764.

8. Datz, Sheldon; and Taylor, Ellison H.: Ionization on Platinum and Tungsten Surfaces. I. The Alkali Metals. J. Chem. Phys., vol. 25, no. 3, Sept. 1956, pp. 389-394.

TABLE I.- COMPOSITION OF EARTH ATMOSPHERE (FROM REF. 5)

Element or compound	Percent by volume	Density at standard temperature and pressure, g/l
Nitrogen	78.08	1.2506
Oxygen	20.95	1.4390
Argon	0.93	1.7837
Carbon dioxide . . .	0.03	1.9767
Neon	1.8×10^{-3}	0.9004
Helium	5.2×10^{-4}	0.1785
Krypton	1.0×10^{-4}	3.708
Hydrogen	5.0×10^{-5}	0.0899
Xenon	8.0×10^{-6}	5.581
Ozone	1.0×10^{-6}	2.220

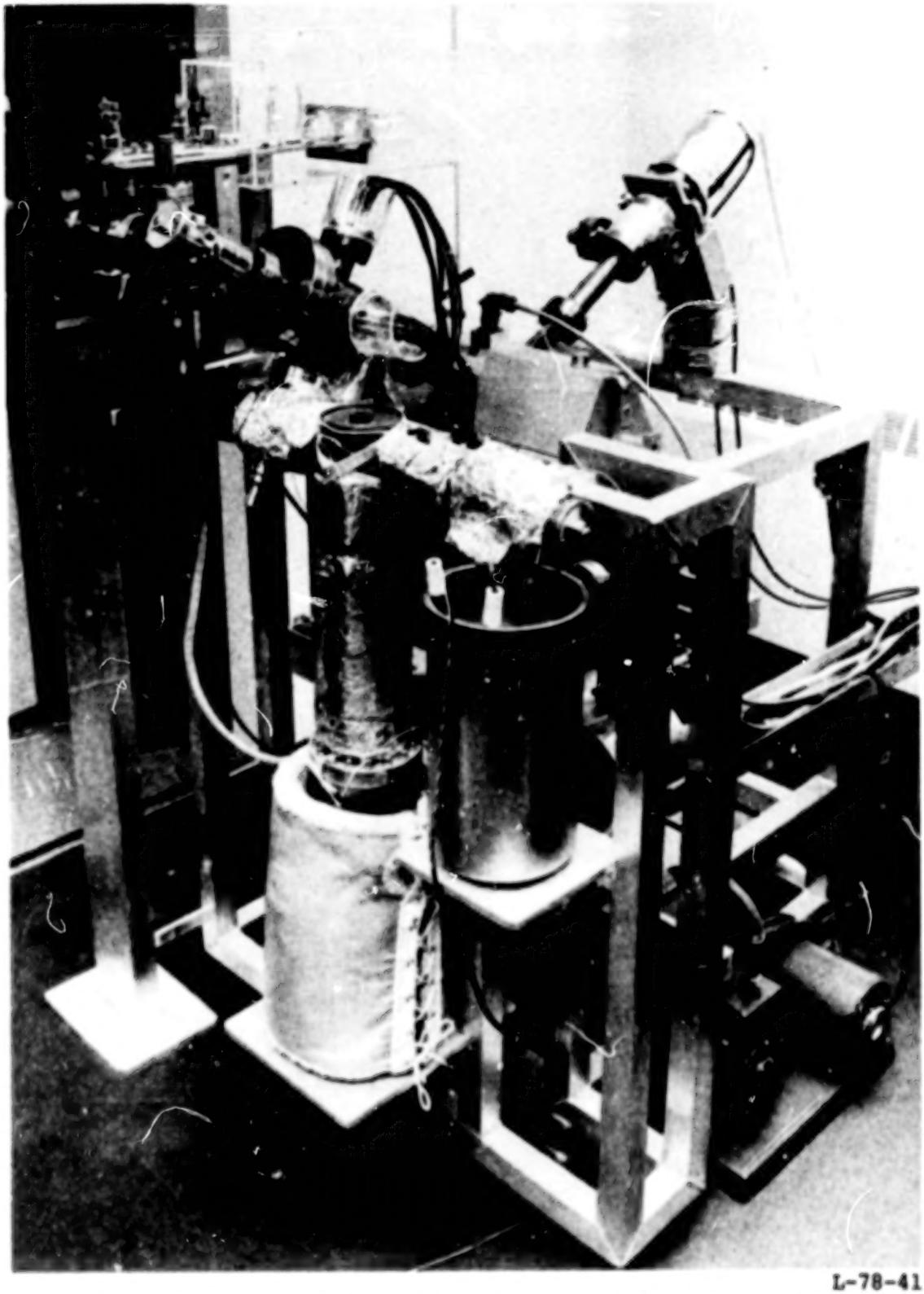

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Figure 1.- Static mode mass spectrometer and vacuum system.

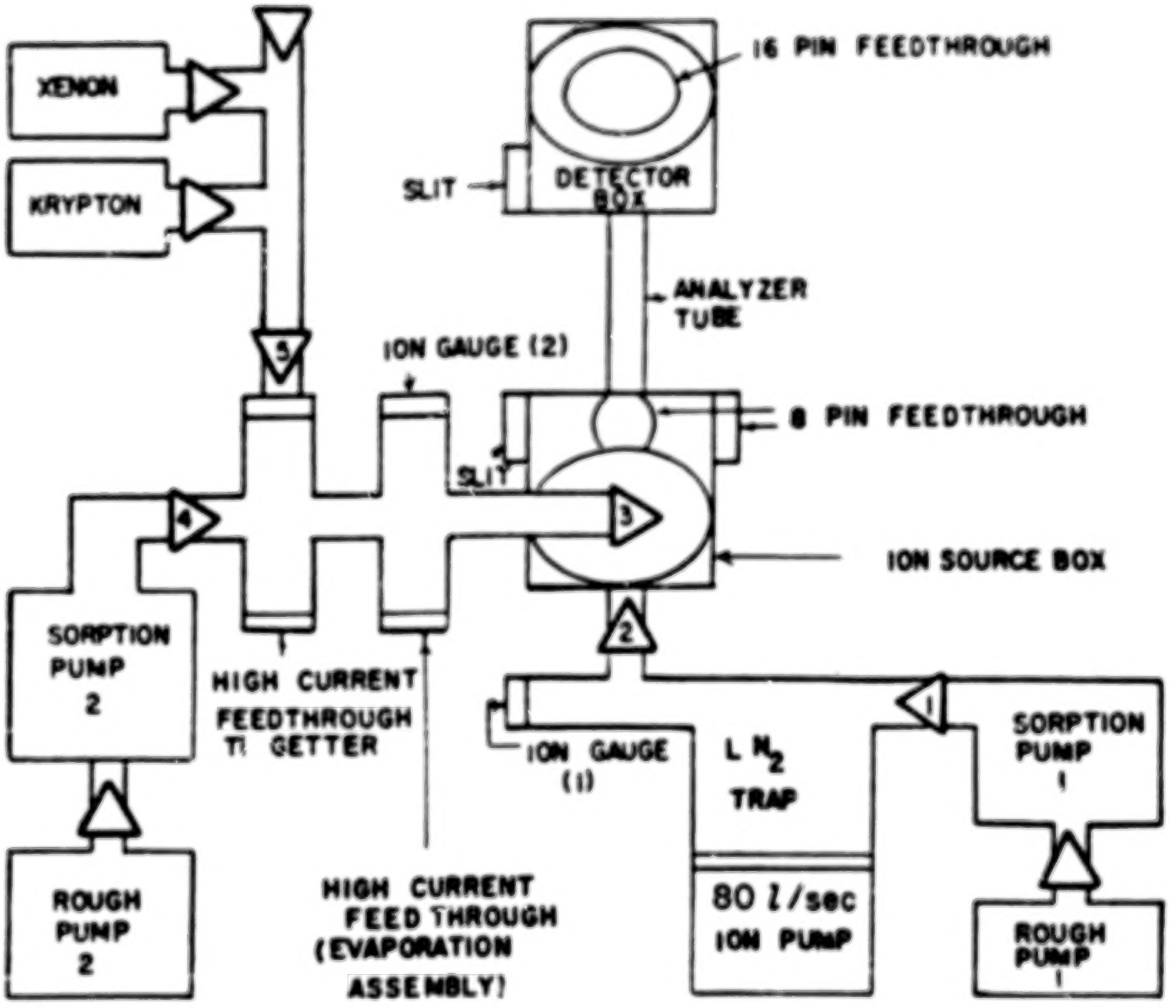

Figure 3.- System block diagram.

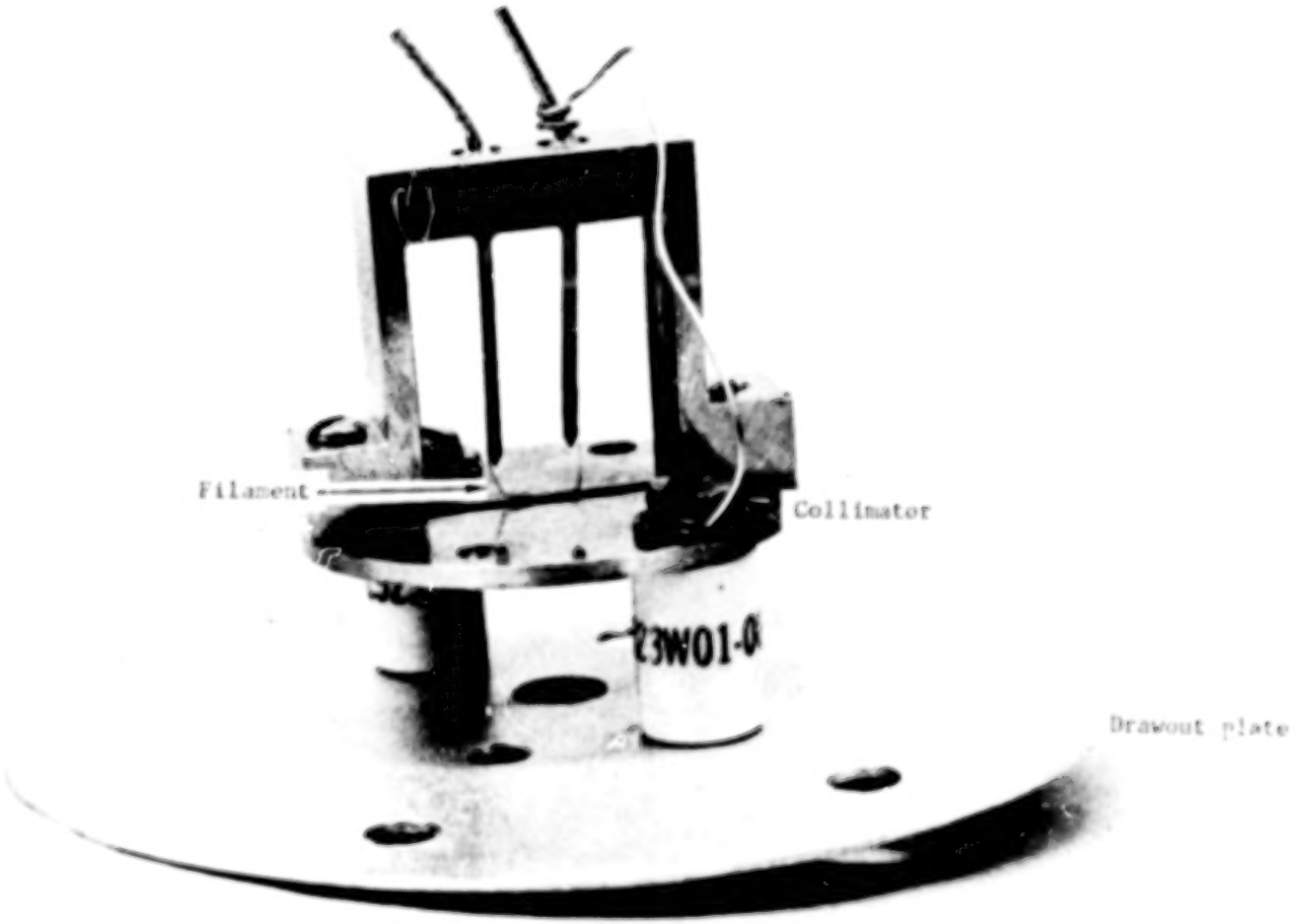

Figure 3.- Thermal ionization source.

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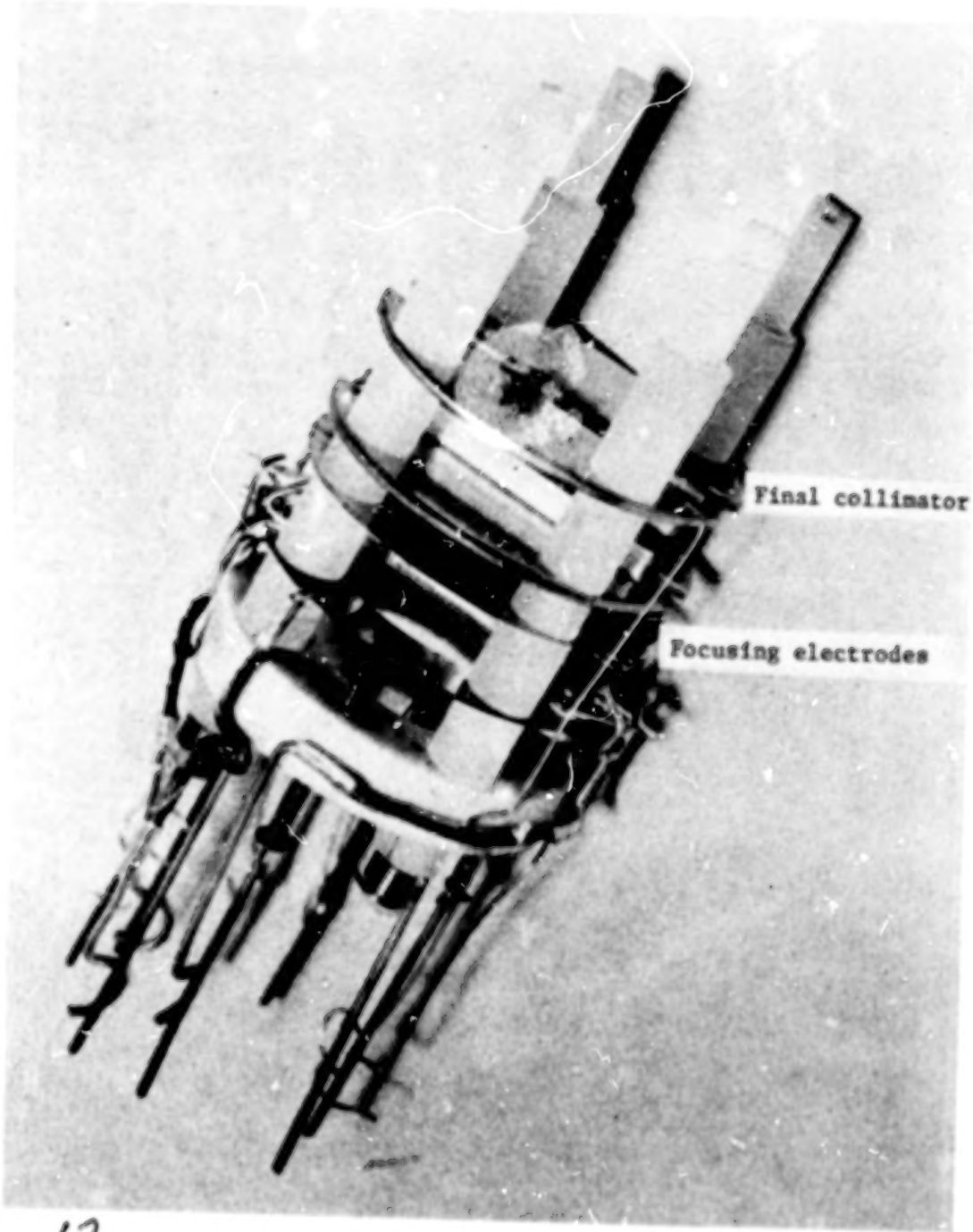

12.

Figure 4.- Electron impact ion source.

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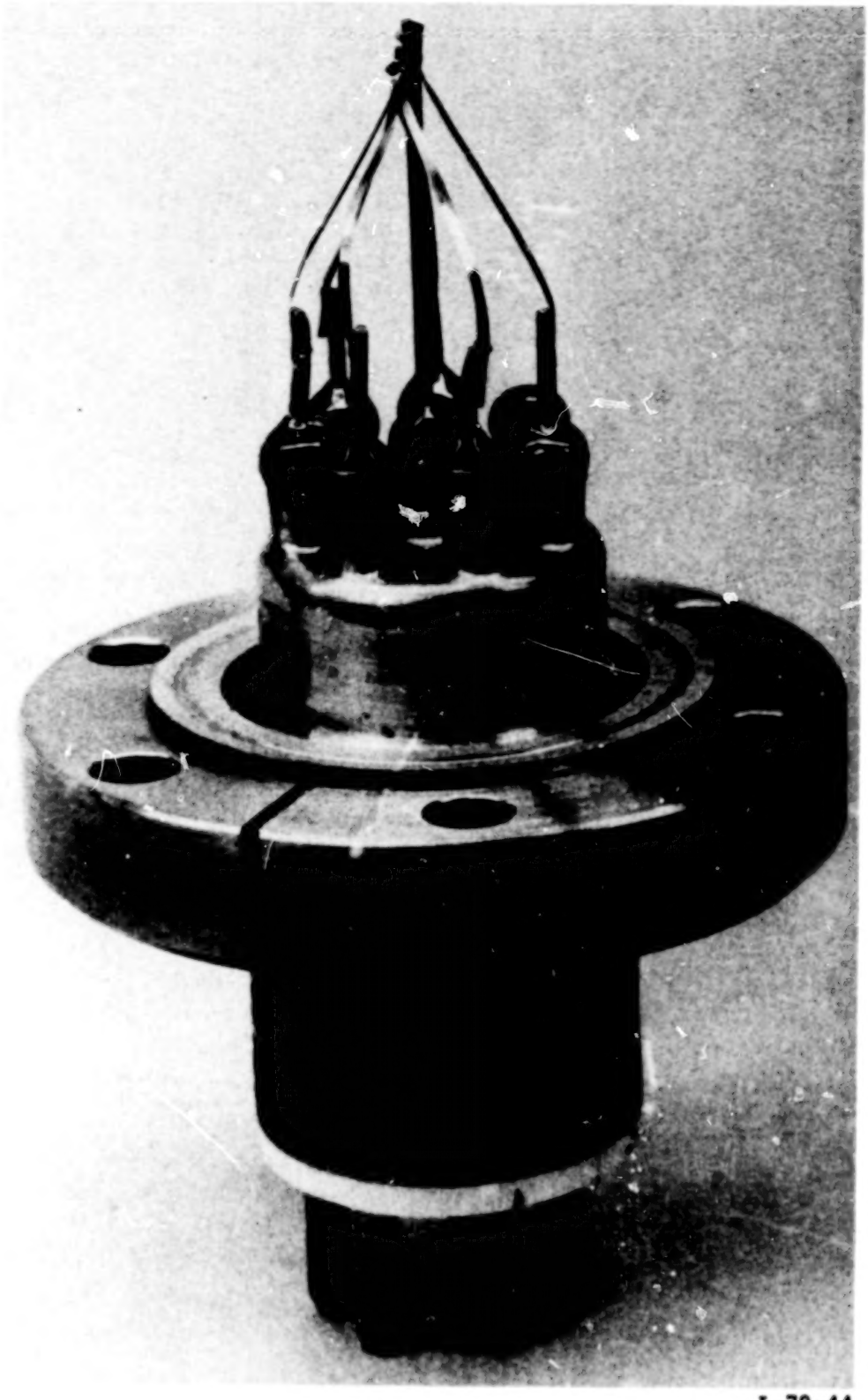

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Figure 5.- Krypton desorption assembly.

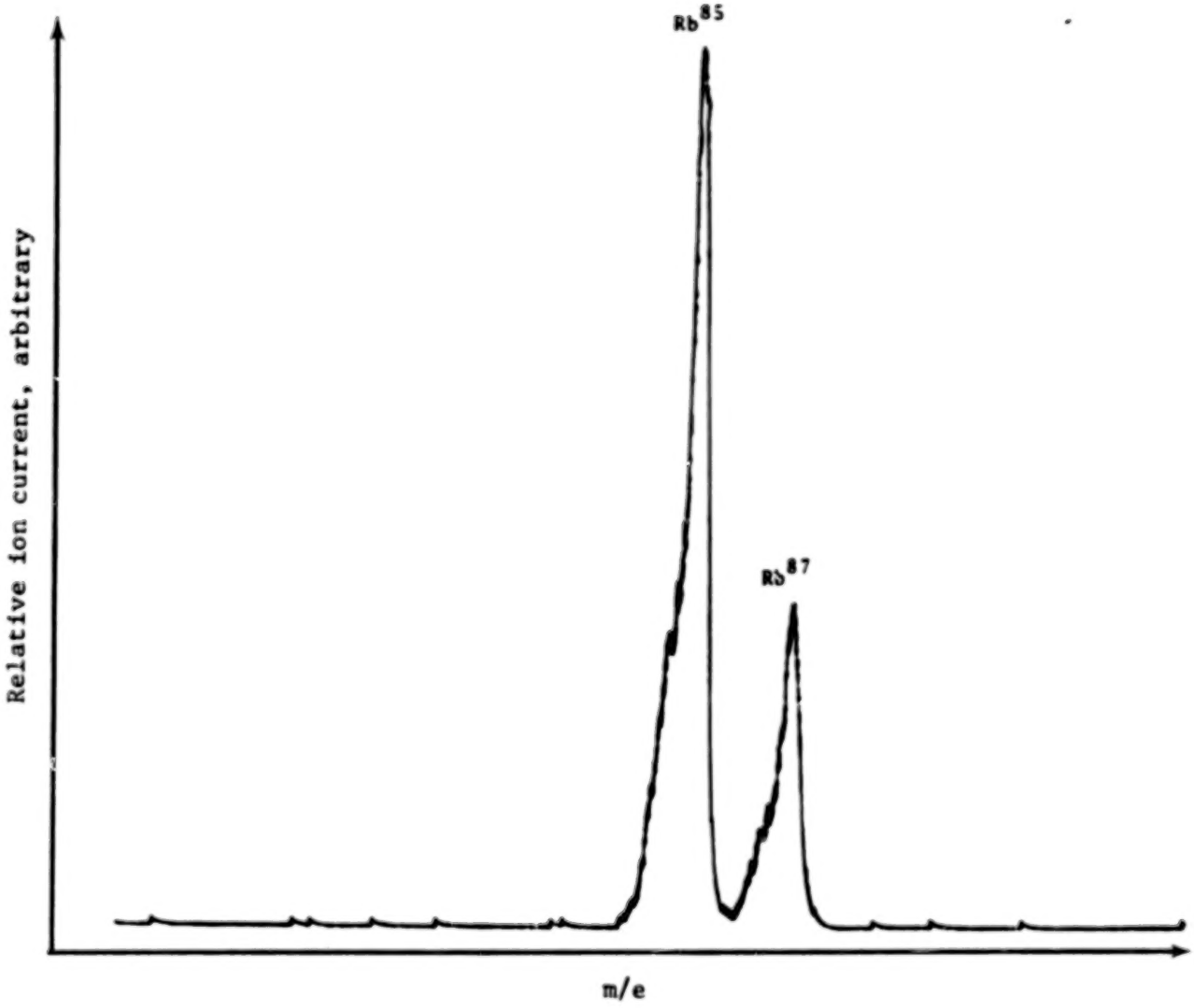

Figure 6.- Mass spectrum of rubidium. m/e denotes mass to charge ratio.

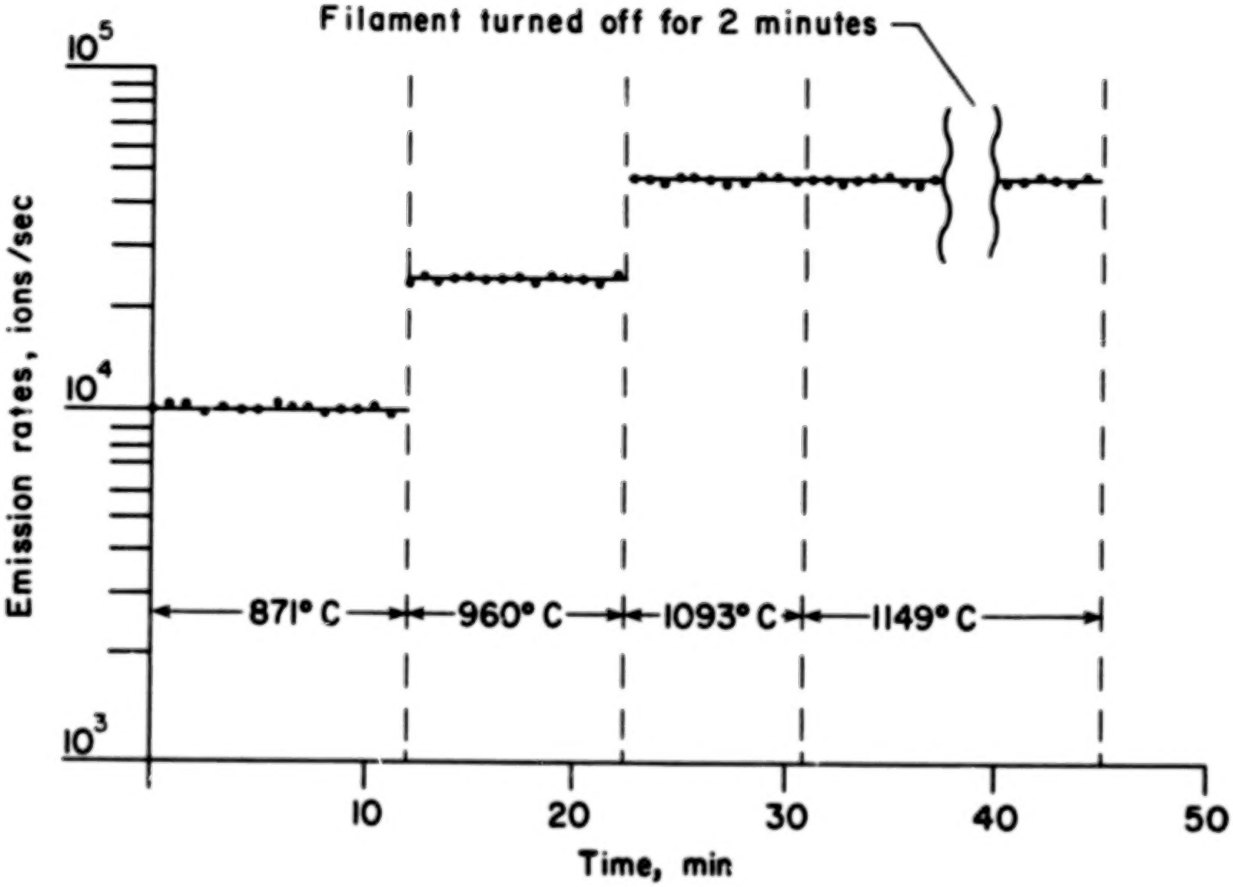

Figure 7.- Ion (Rb^+) emission rates, thermal ionization source.

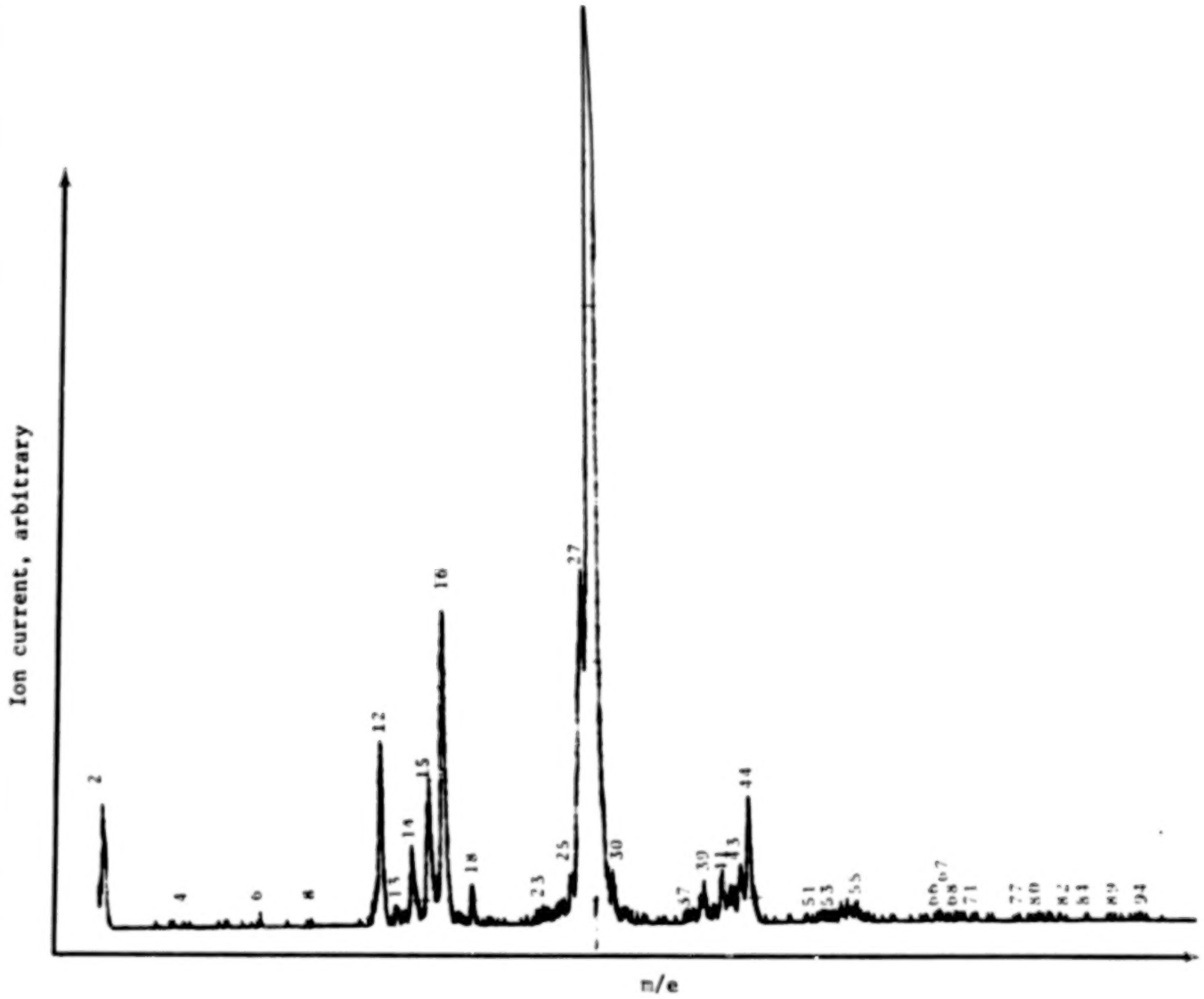

Figure 8.- System background. Electron impact source. m/e denotes mass to charge ratio.

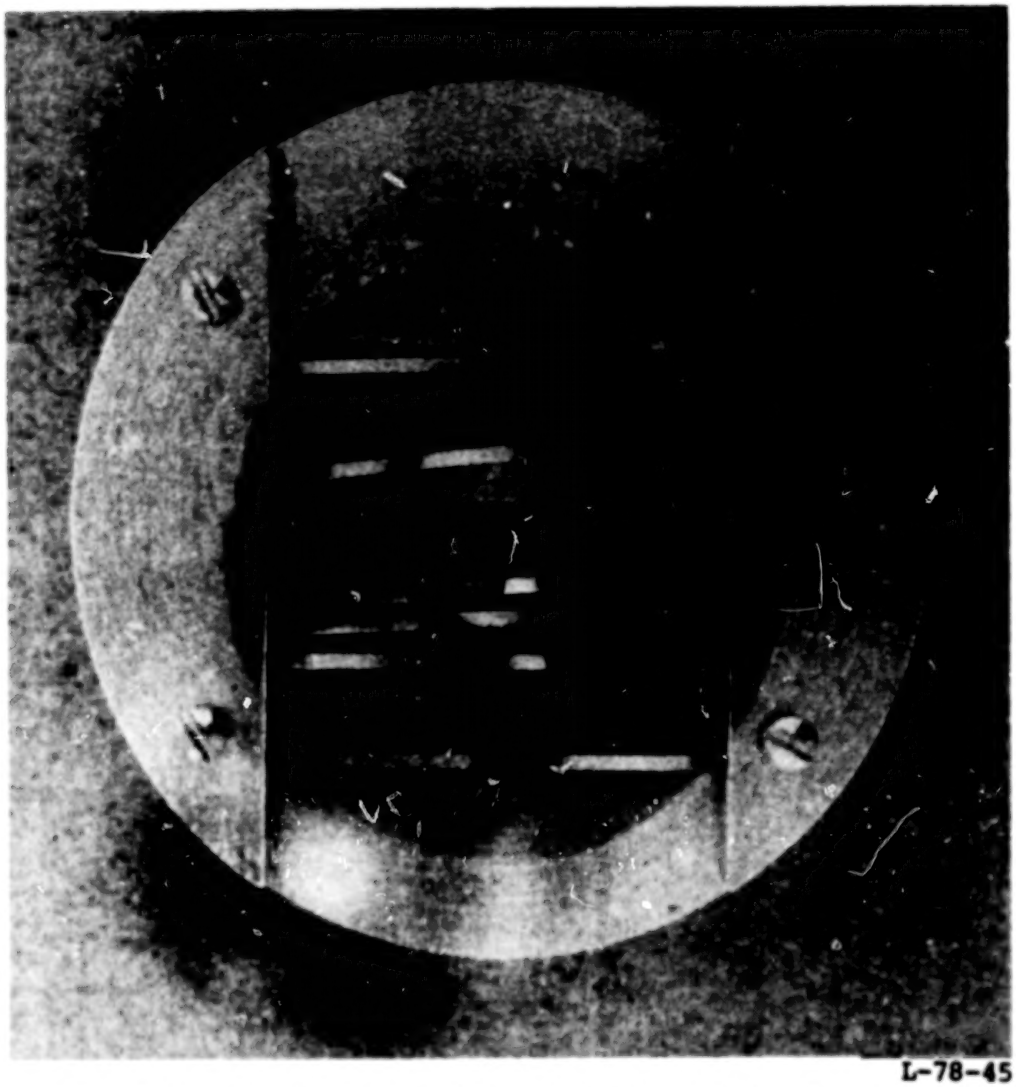

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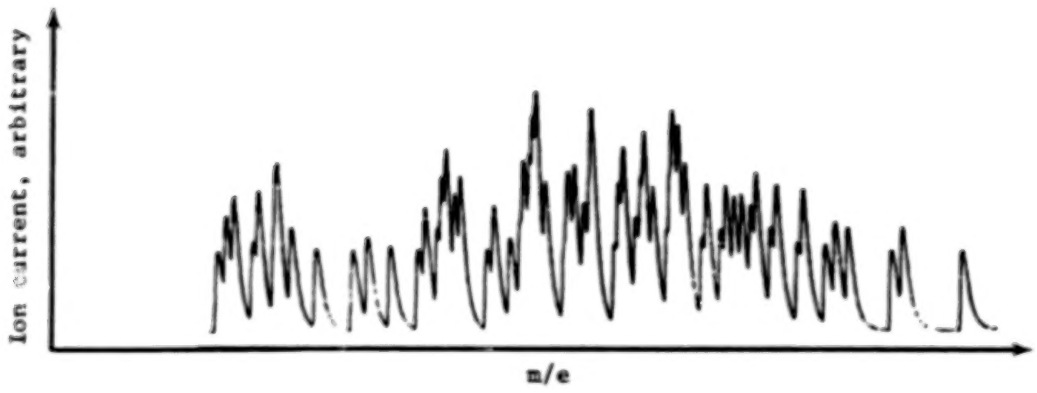
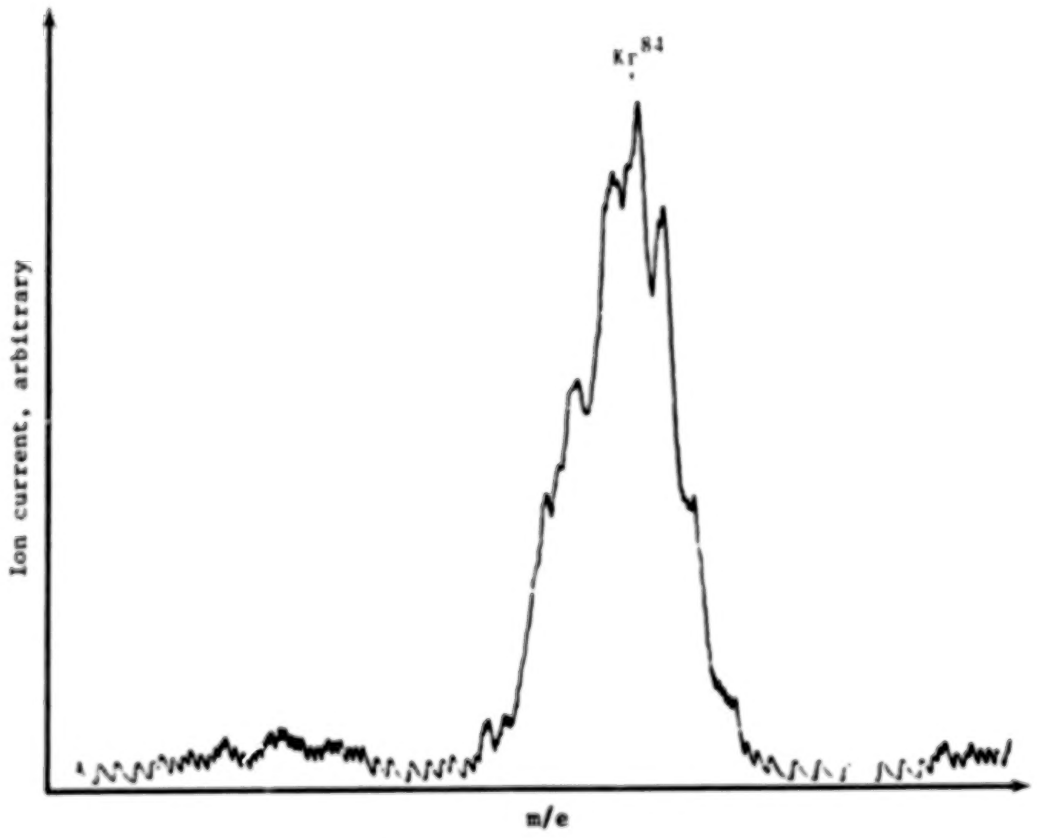
Figure 9.- Gold-plated rhenium filaments prepared for krypton implant.



(a) Pre-emission krypton background spectra.



(b) Post-emission krypton spectra.

Figure 10.- Krypton spectra. m/e denotes mass to charge ratio.

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G. M. Wood: Langley Research Center, Hampton, Virginia.

16. Abstract

An experimental study was undertaken to examine the feasibility of using ion-implanted filaments doped with either an alkali metal or noble gas for in situ recalibration of onboard mass spectrometers during extended space missions. Implants of rubidium and krypton in rhenium ribbon filaments prepared at the NASA Langley Research Center were subsequently tested at Rensselaer Polytechnic Institute in a bakeable 60° sector mass spectrometer operating in the static mode. Surface ionization and electron impact ion sources were both used, each yielding satisfactory results. The metallic implant with subsequent surface ionization provided a means of mass scale calibration and determination of system operating parameters, whereas the noble gas thermally desorbed into the system was more suited for partial pressure and sensitivity determinations.

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